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Key Points:

- Dissolved oxygen depletion induces release of DMS and DMSP from phytoplankton
- Anoxic stress is an important environmental factor affecting marine DMS dynamics
- Ubiquity of anoxic conditions in the coastal oceans suggest global importance

Supporting Information:

- Text S1 and Figures S1 and S2

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Enhancement of dimethylsulfide production by anoxic stress in natural seawater

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Abstract Dimethylsulfide (DMS) is produced by phytoplankton in the ocean and plays an important role in biogeochemical cycles and climate system of the Earth. Previous field studies reported a possible relationship between DMS enhancement and anoxic condition, although the governing processes are still to be identified. Here we show the first direct evidence for the enhancement of DMS production by natural planktonic assemblages caused by anoxic stress. Under the anoxic condition, DMS production was considerably enhanced and DMS bacterial consumption was inhibited, resulting in an eightfold higher rate of gross DMS production than that under the oxic condition. Our results demonstrated that anoxic stress is one of important “environmental factors” in the marine DMS dynamics, suggesting the possible global importance due to ubiquity of anoxic conditions in the coastal oceans. This process would become more important in the future due to expansion of coastal hypoxic and anoxic zones by global warming.

1. Introduction

Dimethylsulfide (DMS) is emitted from the ocean to the atmosphere and plays a key role in the formation of aerosols and clouds in remote marine region [Vallina *et al.*, 2007; Lana *et al.*, 2012]. Aerosols and clouds influence albedo over the oceans and hence have a potential to regulate the radiation budget of the Earth [Charlson *et al.*, 1987], although this remains controversial [Quinn and Bates, 2011]. DMS plays also a key role in the mediation of ecological processes, such as prey detection in marine plankton [Steinke *et al.*, 2006]. The important role of DMS emissions on a global and local scale makes it necessary to evaluate the distribution of DMS in seawater and the controlling factors in DMS release.

DMS concentrations in seawater are determined by complex microbial processes [Stefels *et al.*, 2007]. The major precursor of DMS is dimethylsulfoniopropionate (DMSP), which is produced by many species of phytoplankton [Stefels *et al.*, 2007]. DMS is transformed from DMSP cleavage by bacteria [Moran *et al.*, 2012] and phytoplankton [Niki *et al.*, 2000]. DMSP and DMS production due to microbial metabolism is strongly influenced by environmental factors including salinity [Vairavamurthy *et al.*, 1985; Stefels, 2000], solar radiation [Karsten *et al.*, 1992; Archer *et al.*, 2010; Galí *et al.*, 2011], and nutrients [Stefels, 2000; Sunda *et al.*, 2007]. Recent studies have identified DMS release induced by stress as a key mechanism to control DMS distributions in situ [Toole *et al.*, 2008; Vogt *et al.*, 2010].

Our recent study indicated that anoxic stress is one of the important environmental factors influencing DMS production [Omori *et al.*, 2013]. In an experiment using a bubbling-type equilibrator for the quantification of DMS dissolved in surface seawater, we found that DMS concentrations dramatically increased just after the depletion of dissolved oxygen (DO) in the seawater bubbled with N₂ gas [Omori *et al.*, 2013]. The result indicates that DO depletion triggers an increase in DMS production. If the aerobic microbial community is exposed to anoxic conditions (anoxic stress) in a specific zone, such as the interface between oxic and anoxic seawater and inside of aggregates, they are likely to enhance DMS production and increase DMS levels in response to anoxic stress. There is evidence that the highest DMS concentrations occur just above the oxygen-depleted thermocline in stratified salt pond [Wakeham *et al.*, 1984, 1987; Gibson *et al.*, 1991]. Although anoxic condition inhibits microbial DMS consumption [Wakeham *et al.*, 1987], there is no information about the general relationship of anoxic stress and DMS production.

The objective of this study is to quantitatively evaluate the impact of anoxic stress on DMS production. We examined changes in DMSP/DMS dynamics under oxic and anoxic conditions. The majority of DMSP is degraded to methanethiol (MeSH) as one of end products of bacterial demethylation/demethiolation in natural seawater [Kiene, 1996; Kiene and Linn, 2000a, 2000b]. A smaller proportion of DMSP (approximately 10%) is cleaved to DMS and acrylate. In this study we report production rates of DMS and MeSH that were determined using isotopically labeled DMSP. Since some studies have demonstrated biological reduction of dimethylsulfoxide (DMSO) as a source of DMS under anaerobic conditions [Hatton *et al.*, 1994], we also investigated whether DMS was produced from DMSO in anoxic seawater.

2. Methods

Surface seawater was sampled from Tokyo Bay (35°39'N, 139°46'E) and the coastal site (34°39'N, 138°57'E) in Oura Bay located on Izu Peninsula, Japan, in August 2014 (Figure S1 in the supporting information). The Tokyo Bay is an area with high concentrations of nutrients and biomass [Koibuchi *et al.*, 2000]. In contrast, the coastal area is strongly influenced by the open sea and there are less microbial organisms at this sampling site than in the bay water. The samples were collected with a clean bucket and prefiltered through a 100 μ m nylon mesh screen to remove macrozooplankton. Then, they were transported within 2–12 h to our laboratory, where the experiments were conducted. For the determination of phytoplankton composition, the pigment analysis was made with high-performance liquid chromatography.

Similar to Omori *et al.* [2013], we conducted bubbling experiments using an equilibrator combined with proton transfer reaction-mass spectrometry (PTR-MS) to examine the rates of change in DMS and MeSH in seawater (for experimental details, see the supporting information). In brief, the seawater samples in a glass equilibrator were bubbled with gas. Dissolved DMS and MeSH were extracted to gas phase and detected to PTR-MS. Air and N₂ were used as bubbling gases to create oxic and anoxic conditions for the seawater sample.

The rates of DMS and MeSH production and consumption were quantified using isotopically labeled materials in the bubbling experiments. The change in bulk concentrations of DMS and MeSH in the equilibrator bubbled with air or N₂ for 1.5 or 2 h was measured as net production rates. After 60 or 90 min bubbling with air or N₂, DMSP-d6 and DMS-d3 were simultaneously added into the equilibrator. The increase rates of DMS-d6 and MeSH-d3 from DMSP-d6 were measured as DMS production from DMSP cleavage and MeSH production from demethylation/demethiolation of DMSP. The DMS-d3 decrease was evaluated as gross DMS consumption. Triplicate and double experiments were made using the bay and coastal seawater samples, respectively. In addition, bubbling experiments adding DMSO-d6 were conducted to measure the DMS-d6 increase as DMSO reduction.

The concentrations of total and dissolved DMSP (DMSPt and DMSPd) were determined using purge technique combined with PTR-MS at the beginning, just after addition of isotopically labeled materials and at the end of each experiment, referring to Stefels *et al.* [2009]. The particulate DMSP (DMSPp) concentration was calculated by subtracting the DMSPd from the DMSPt concentration.

We calculated the DMS dynamics taking into account various pathways including DMS production derived from DMSP cleavage, DMSO reduction and particle release, and gross DMS consumption and production, referring to Asher *et al.* [2011]. To scale the increase rate of DMS-d6 to the DMS production rate, the increase rate was divided by the concentration of added DMSP-d6 and multiplied by the DMSPd concentration in the seawater sample. Similarly, the decrease rate of DMS-d3 was scaled to the DMS consumption rate using DMS concentration. Summing of the net production (bulk DMS increase) rate and the consumption rate yielded the rates of gross DMS production. We constructed a simple mass balance equation, which assumes that the gross DMS production equals the amount of DMSP cleavage, DMSO reduction, and DMS release from biological particulate [Asher *et al.*, 2011]. The DMS release might include a part of the conversion of DMSP and DMSO released from biological cells into the seawater other than direct DMS excretion.

3. Results and Discussion

Chlorophyll *a* concentration as an index of phytoplankton biomass was more than tenfold higher in the Tokyo Bay water (28 μ g L⁻¹) than in the coastal seawater (2.0 μ g L⁻¹). Pigment analysis detected several

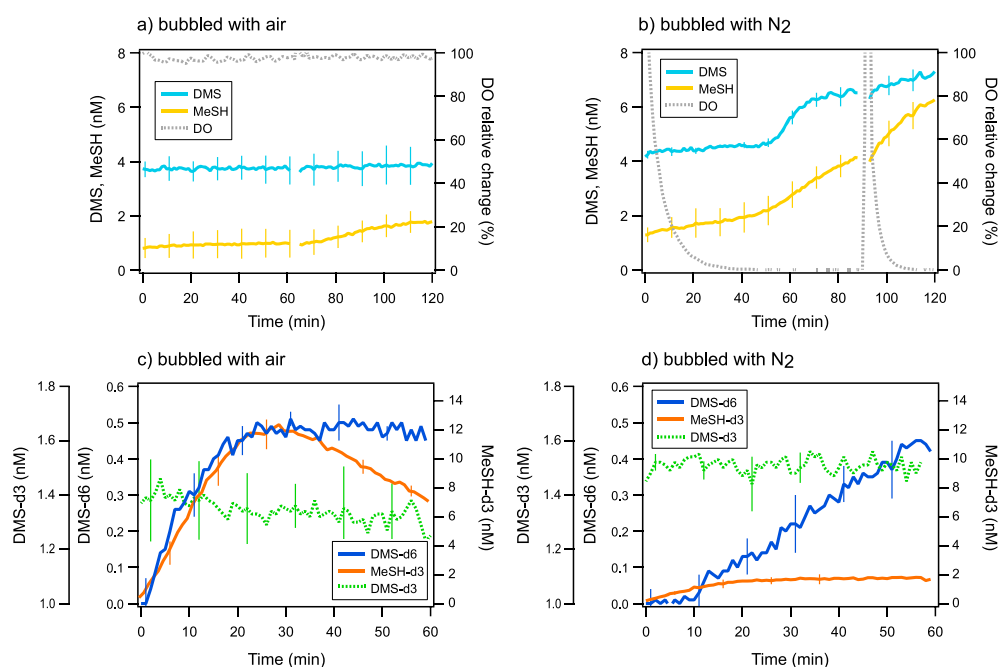


Figure 1. Time course of changes in DMS and MeSH concentrations (nM) and relative DO concentration (initial concentration = 100%) in Tokyo Bay water bubbled with (a) air and (b) N_2 , and changes in concentrations of DMS-d6, MeSH-d3, and DMS-d3 in the bay water bubbled with (c) air and (d) N_2 . For Figures 1c and 1d, the x axes are elapsed time after the addition of DMSP-d6 and DMS-d3. Values are 1 min averages. The error bars represent the standard deviation of triplicates.

pigments in the bay water; fucoxanthin ($9.5 \mu\text{g L}^{-1}$), peridinin ($1.2 \mu\text{g L}^{-1}$), and alloxanthin ($0.2 \mu\text{g L}^{-1}$), which are known as marker pigments indicating the presence of diatoms, dinoflagellates, and cryptomonads, respectively. Fucoxanthin ($0.3 \mu\text{g L}^{-1}$) and 19-hexanoyloxyfucoxanthin ($0.04 \mu\text{g L}^{-1}$) were detected in the coastal seawater, indicating the presence of diatoms and haptophytes. Among these algae, dinoflagellates and haptophytes are known as algae with DMSP-lyase capacity, as previous studies have suggested [Stefels *et al.*, 2007].

Figure 1 shows the changes in DMS and MeSH concentrations over time in the bay sample bubbled with air or N_2 . For oxic seawater bubbled with air, the DMS concentration remained constant ($3.8 \pm 0.070 \text{ nM}$) during the course of the experiment. The MeSH concentration was stable for the first 1 h. After the addition of DMSP-d6 and DMS-d3, the MeSH started to slightly increase at a rate of $0.46 \pm 0.029 \text{ nM h}^{-1}$ (Figure 1a), implying that the isotopically labeled materials might stimulate dimethylation/dimethiolation processes by microbial metabolism. With N_2 as the bubbling gas, the DO concentration in the equilibrator declined continuously and was depleted within 50 min from the start of bubbling (Figure 1b). After DO depletion, the DMS concentration started to increase more rapidly at rates of $2.0 \pm 0.34 \text{ nM h}^{-1}$. The MeSH concentration started to increase before 50 min with a lower rate, and the increase became more drastic after 50 min at a rate of $3.2 \pm 0.52 \text{ nM h}^{-1}$. The DO increase at around 90 min was caused by the addition of DMSP-d6 and DMS-d3 into the equilibrator. After the addition, DMS and MeSH continued to increase at the same rates under the anoxic condition. Changes in the DMS and MeSH concentrations in the coastal seawater were similar to those in the bay seawater (Figure S2 in the supporting information), in spite of the difference in their initial concentration and phytoplankton abundance.

The concentrations of DMS-d6, MeSH-d3, and DMS-d3 were monitored after the addition of DMSP-d6 and DMS-d3 into the bay seawater (Figures 1c and 1d). In the oxic seawater, DMS-d6 and MeSH-d3 derived from DMSP-d6 quickly started to increase at rates of 0.85 ± 0.024 and $27 \pm 1.4 \text{ nM h}^{-1}$, respectively, and the concentrations reached their peaks around 20–30 min after the addition (Figure 1c). The sum of the maximum concentrations of DMS-d6 and MeSH-d3 was almost the same as the concentration of the added DMSP-d6 (104%). This implies that the products of DMSPd degradation are only DMS and MeSH (3:97). Kiene and Linn [2000a] reported, however, that a large proportion of metabolized DMSP is

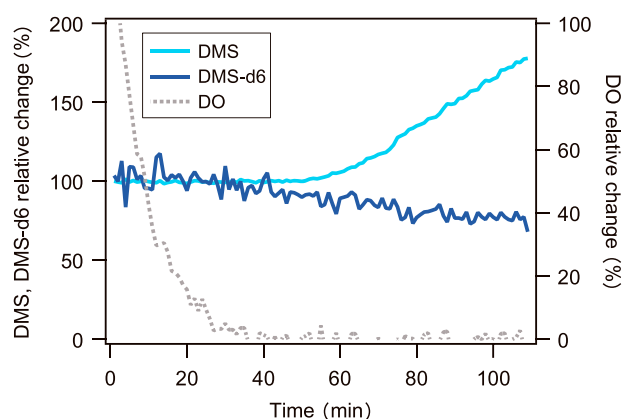


Figure 2. Time course of the relative concentrations of DMS, DMS-d6 (%), and DO (initial concentration = 100%) in the coastal seawater with added DMSO-d6 bubbled with N_2 .

respectively (Figure 1d), which were significantly lower than those in the oxic seawater ($P < 0.05$; Mann-Whitney U-test). This indicates that both DMSP cleavage and demethylation/demethiolation are suppressed under the anoxic condition. DMS-d3 concentration decreased at a rate of $0.053 \pm 0.024 \text{ nM h}^{-1}$ in the oxic seawater, while DMS-d3 did not decrease in the anoxic seawater ($0.013 \pm 0.015 \text{ nM h}^{-1}$) (Figures 1c and 1d). This suggests that DMS consumption is also prevented under the anoxic condition. In the coastal seawater, no increase in MeSH-d3 and no decrease in DMS-d3 were also observed under anoxic condition (Figures S2c and S2d in the supporting information).

In order to investigate the DMS production from DMSO under the anoxic condition, isotopically labeled DMSO was added to the coastal seawater (Figure 2). After the DO depletion in the seawater bubbled with N_2 , the unlabeled DMS concentration started to increase and reached 180% of the initial value. The DMS-d6 derived from DMSO-d6 did not increase over time. The same result was observed in the investigation

transformed to a nonvolatile dissolved product and a portion is assimilated into cell protein. Here the added DMSP-d6 concentrations are higher than the dissolved DMSP concentrations in situ (Figure 3). The high level of DMSP-d6 might stimulate DMSP catabolism and might be immediately transformed to 100% isotopically labeled MeSH and DMS as shown in Figure 1c. There is also a possibility that the rates of demethylation/demethylation and DMSP cleavage are overestimated due to the stimulation of bacterial activity.

DMS-d6 and MeSH-d3 in the anoxic seawater gradually increased over time at rates of 0.52 ± 0.060 and $1.9 \pm 0.28 \text{ nM h}^{-1}$,

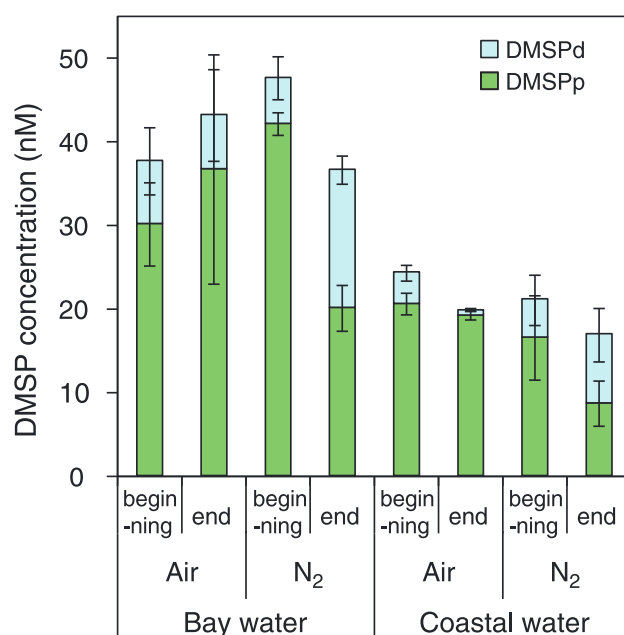


Figure 3. Concentrations of DMSPp and DMSPd (nM) in seawater bubbled with air and N_2 at the beginning and end of the bubbling experiments. The error bars represent the standard deviation of triplicates in the bay water and the range of duplicates in the coastal water.

of the bay water samples. These findings clearly indicate that the DMS increase under the anoxic condition was not due to DMSO reduction.

Figure 3 illustrates the concentrations of DMSPp and DMSPd at the beginning and the end of the experiments. In the bay water bubbled with air, the concentration of particulate and dissolved DMSP showed no significant changes between the beginning and the end of the experiments. The DMSPp concentration decreased by half, and the DMSPd concentration increased threefold in the bay water bubbled with N_2 . In the coastal seawater under the anoxic condition, a decrease in DMSPp and an increase in DMSPd were also observed (Figure 3). The significant changes in both DMSPp and DMSPd concentrations ($P < 0.05$; Mann-Whitney U-test) suggest that DMSP contained in algae (or other particles) is released to seawater in response to the change from oxic to anoxic condition.

Table 1. Rates of DMS Production and Consumption in the Bubbling Experiments

Rate (nM h^{-1})	Bay Water		Coastal Water		Estimate of Each Rate
	Oxic	Anoxic	Oxic	Anoxic	
Net production	0.094 ± 0.20	2.0 ± 0.34	0.0063 ± 0.0091^a	1.6 ± 0.034^a	DMS increase rate
DMS consumption	0.14 ± 0.049	-0.071 ± 0.083	0.10 ± 0.058^a	0.014 ± 0.062^a	DMS-d3 decrease rate
Gross production	0.24	1.9	0.11	1.6	Sum of net production rates and consumption rates
DMSP cleavage	0.23 ± 0.037	0.71 ± 0.15	0.011 ± 0.0033^a	0.31 ± 0.20^a	DMS-d6 increase rate from DMSP-d6
Particle release	0.01	1.2	0.10	1.3	Difference of gross production rate and DMSP cleavage rate

^aThe range of each rate for the coastal waters shows the range of two replicates.

Table 1 shows the rates of DMS consumption and production obtained by the isotope approach. The rates of gross DMS production in the bay and coastal seawater were eightfold and fifteenfold higher under the anoxic condition than under the oxic condition, respectively. The gross DMS production rate under the anoxic condition (approximately 2 nM h^{-1}) was considerably higher than gross (or net) DMS production rates in shelf and coastal areas ($0.03\text{--}0.4 \text{ nM h}^{-1}$ [Slezak *et al.*, 2007; Galí *et al.*, 2011]) and the algal bloom region ($0.01\text{--}0.6 \text{ nM h}^{-1}$ [Simó and Pedrós-Alió, 1999; Lizotte *et al.*, 2008]). Meanwhile, the DMS consumption rates declined nearly to 0 under the anoxic condition (Table 1), because anoxic condition inhibits DMS bacterial consumption [Wakeham *et al.*, 1987; Jonkers *et al.*, 1998; Lomans *et al.*, 1999]. These results suggest that when aerobic microbial community is exposed to anoxic stress, the enhancement of DMS production and the inhibition of DMS consumption rapidly raise DMS levels in the seawater. The DMS peak formed at the interface between the oxic and anoxic layers [Wakeham *et al.*, 1984, 1987] would be explained by the enhanced DMS production due to anoxic stress.

Since there was no DMSO reduction in these experiments (Figure 2), the direct DMS release from biological particles (algal lysis) was calculated as the difference between the gross production rate and DMSP cleavage rate (Table 1). Both DMSP cleavage and DMS release were enhanced under the anoxic condition. In particular, the DMS release rates under the anoxic condition were more than tenfold higher than those under the oxic condition, and the DMS release dominated DMS production, accounting for 79% and 63% in the bay and coastal water, respectively. In addition, the DMSP cleavage rates were higher under the anoxic condition than under the oxic one. While the DMS-d6 production from DMSP-d6 was inhibited under the anoxic condition (Figures 1c and 1d), the high DMSPd concentration due to phytoplankton release (Figure 3) seems to have raised the DMSP cleavage rates.

The pathways of DMS production were clearly different between the oxic and anoxic condition in the bay water (Table 1). The relative quantitative flows of DMS production and DMSP transformation are described in Figure 4. While almost all DMS was derived from DMSPd cleavage (99%) under the oxic condition, the DMS production under the anoxic condition was mainly due to direct release of DMS from phytoplankton (63%). In addition, the DMS production was contributed by DMSP cleavage (37%) via dissolved DMSP release from phytoplankton in response to the anoxic condition (Table 1 and Figure 2). These results indicate that DMS and DMSP release from phytoplankton are an important source of DMS under anoxic conditions. If phytoplankton suffers from anoxic stress, it might emit DMSP and DMS into the seawater, resulting in a rise of DMS levels.

The stress-induced release of DMS and DMSP from phytoplankton is a physiological reaction. Two explanations have been proposed. One is the overflow hypothesis, which states that DMSP and DMS serve as overflow metabolites when phytoplankton undergoes unbalanced growth [Stefels, 2000; Sunda *et al.*, 2007]. Another is the antioxidant hypothesis, which suggests that some products of DMSP, including DMS, could act as intracellular scavengers of reactive oxygen species (ROS) [Sunda *et al.*, 2002]. It is little known how anoxic condition affects the physiological processes, such as respiration and photosynthesis, in phytoplankton cells [Wu *et al.*, 2012]. In mammal cells, hypoxia and anoxic condition induce ROS formation to regulate respiration processes [Turrens, 2003; Clanton, 2007]. The release of ROS to cytosol in mitochondria is indicated to play a role as O_2 sensors under hypoxic condition [Guzy *et al.*, 2005; Guzy and Schumacker, 2006]. If phytoplankton is exposed to anoxic condition, the ROS production in their cells might be changed. In order to regulate the radical concentration, phytoplankton might release DMS and DMSP to the seawater. The elucidation of the mechanisms of DMS release would help to better understand the physiological role of DMS and DMSP in phytoplankton.

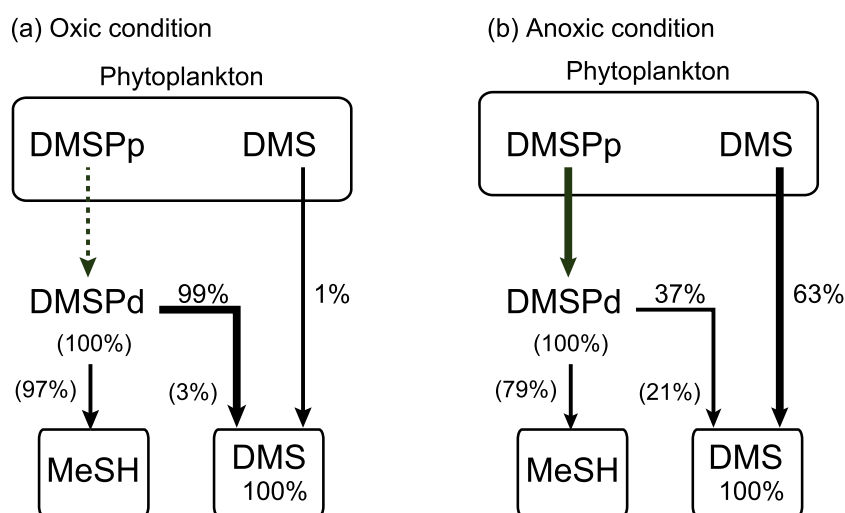


Figure 4. Diagrams of the paths and fates of DMS production and DMSP degradation under oxic and anoxic conditions in the bay water. The quantitative flows to DMS (100%) are the ratio of DMS release and DMSP cleavage in gross DMS production (Table 1). The partitions of MeSH and DMS from DMSPd (100%), estimated based on the ratio of increase rates of MeSH-d3 and DMS-d6 derived from DMSP-d6, are given in parenthesis.

The quantitative flows of DMSPd to DMS and MeSH were different under the oxic and anoxic conditions (Figure 4). The partition of MeSH derived from DMSPd under the anoxic condition was lower (79%) than that under the oxic condition (97%). In contrast, the partition of DMS was higher under the anoxic condition (21%) than under the oxic one (3%). The lower fraction of MeSH was probably caused by more suppression of demethylation/demethylation of DMSPd by bacterial metabolism than DMSP cleavage due to the anoxic condition (Figures 1c and 1d). MeSH is known as a main product of DMSP in natural seawater [Kiene, 1996; Kiene and Linn, 2000a]. This is probably because DMSP via MeSH serves as a major source of reduced sulfur for bacterioplankton in aerobic seawater [Kiene *et al.*, 1999]. Using tracer experiments, Kiene and Linn [2000a] hypothesized that when DMSPd is available in excess over immediate bacterial sulfur demand, a shift in biogeochemical fate takes place from degradation to MeSH toward DMS and nonvolatile sulfur compounds. Under the anoxic condition, where aerobic bacterial activity is expected to be lower than that under the oxic condition, DMSPd conversion by bacterial metabolism would change from MeSH production to DMS.

Global climate change causes ocean warming, increase of stratification, and large changes in rainfall patterns, which would lead to a decrease in O_2 concentrations in the ocean [Keeling *et al.*, 2010] and to an expanded hypoxic/anoxic zone in coastal areas [Diaz and Rosenberg, 2008]. Our study suggests that anoxic stress plays an important role as an environmental factor increasing the DMS concentration. At present, the coastal hypoxic/anoxic zones are associated with major population centers and the watersheds deliver large quantities of nutrients [Diaz and Rosenberg, 2008]. If the hypoxic/anoxic zones are expanded due to the enhancement of stratification and increase of river discharge with high concentrations of nutrients, the layer with high DMS level is likely to expand. The high-DMS layer will be formed just above the hypoxic/anoxic water mass. Although the high level of DMS does not directly influence the enhancement of DMS emissions to the atmosphere, it might increase the DMS concentration throughout the water column. An understanding of DMS and DMSP dynamics in the upper layer of anoxic water will become more important for the evaluation of global DMS distributions in the future. Further studies are required to be able to quantify the contributions from anoxic stress to DMS concentrations in the seawater.

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